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SOLID PHASE EXTRACTION OF POLYAROMATIC HYDROCARBONS
FROM DRINKING WATER.

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The use of solid phase extraction (SPE) for the analysis of polyaromatic hydrocarbons in water has been investigated. Current methodology involves the liquid liquid extraction (LLE) of the PAHs using dichloromethane followed by quantitation by HPLC with fluorescent detection. This research project was undertaken in order to develop a method that would allow the simplification of existing techniques, reduced use of toxic solvents, greater reproducibility, increased operator throughput, decreased storage and shipping costs, and that would be more amenable to the introduction of robotics.

The study began with the examination of phenyl, cyclohexyl, octadecyl and cyanopropyl phases using ethyl acetate and iso-octane as the eluting solvent. All phases were acceptable (but for convenience the octadecyl phase was selected for detailed examination) and iso-octane was the better eluting solvent.

Products from five different manufacturers (Baker, Supelco, Analytichem, Alltech and Waters) were evaluated and found to be comparable. Five different Lot Numbers from one manufacturer (J. T. Baker) were examined and all lots were found to give acceptable results.

The recoveries were found to be consistent over a twenty fold range of concentrations, e.g., from 125 to 2500 ng/L in the case of pyrene.

PAHs were shown to be stable, when adsorbed onto octadecyl SPE columns, by storing columns with adsorbed analytes for periods of up to three months at room temperature.

The recoveries of PAHs from four different natural waters (Verner raw water, Lakeview raw water, Ottawa City tap water and a drilled rural well) and one reference water (supplied by Dr. Brian Hollebone of Carleton University) were determined. It was found that with a matrix other than tap water the recoveries were very low, <20% in some cases, when iso-octane is used as the eluting solvent. The poor recoveries were likely caused by the multitude of phases present, preventing the interaction between iso-octane and adsorbed analytes. This situation was easily corrected by eluting, first, with a small volume of acetonitrile followed with iso-octane. The acetonitrile replaced the water and, being miscible with both water and iso-octane, allowed a more efficient elution.

In order to simplify the method, the effect of alternative eluting solvents were ascertained. Ten ml of iso-octane were required for complete elution of analytes from 500 mg columns and the solvent then had to be evaporated prior to quantitation. Acetonitrile (3 mL) and, alternatively, toluene (3 mL) were used to elute adsorbed analytes, followed by direct injection of the eluate onto the HPLC. Recoveries were low for the higher molecular weight compounds when acetonitrile was used and low for the low molecular weight compounds when toluene was used. Replacement of iso-octane with pentane, which is more easily volatilized, gave excellent recoveries for all the PAHs including naphthalene.

Interfering substances were not a problem, throughout the project, when quantitation was by HPLC with a fluorescent detector.



Breakthrough Volumes:

The possibility that adsorbed analytes might be desorbed from the column during passage of the sample was investigated by adsorbing small amounts of a PAH (e.g., 10 ug of anthracene) onto a 500 mg octadecyl column, pumping 1940 ml of water through the column at a flow rate of 5 ml/min using an HPLC, and monitoring the passed water with a fluorescent detector. Under these conditions breakthrough would have easily been seen at the 10 ng/mL (10 ug/L) level in the passed water and no evidence of anthracene in the passed water was found. Thus, we can conclude that, for this quantity of anthracene, even after the passage of more than twice the amount of water present in one sample (800 ml), that breakthrough, if it occurs, is less than one thousandth of the quantity of adsorbed analyte per mL of passed water. Similar results were obtained for fluoranthene.

Conclusions:

The use of solid phase extraction for the analysis of PAHs in water is a feasible analytical technique allowing the quantitation of PAHs including naphthalene from drinking water. Neither breakthrough of analytes, nor interferences when using HPLC with fluorescent detection, are a problem with the methodology developed. Further research should include work to further simplify the elution process. Approaches might include:

- 1) the use of 200 mg columns (which have a smaller bed volume thereby allowing complete elution with a smaller volume of solvent than the 500 mg size), elution with acetonitrile, followed by direct injection, or
- 2) replacement of the highly retentive C-18 phase with C-8 or C-2, or another less retentive phase to allow direct acetonitrile elution.